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主 論 文 の 要 旨

論文題目　Study on Gas/Liquid Pulsed Discharge Plasma in a Slug Flow Reactor for Nanoparticles Synthesis and Dye Decomposition
(気液スラグ流反応器内でのパルス放電プラズマによるナノ粒子合成及び染料分解に関する研究)

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論 文 内 容 の 要 旨

This study focused on the pulsed discharge plasma in a slug flow system for the synthesis of metal oxide nanoparticles and the decomposition of organic dyes. Compared with traditional methods to produce gas/liquid plasma, the slug flow system provided a continuous and stable reaction field, beneficial for generating stable plasma and synthesizing nanoparticles. During the process, toxic solvents and ligands were not required, decreasing the operating cost and environmental stress. Hence, the system was applied to various reaction processes to create new applications and to examine its advantages. In addition, this system was firstly implemented under pressurized argon. The insight into the chemical properties of the system was investigated under pressurized conditions, and the effect of pressure on the system was also studied.

In Chapter 1, the general properties of plasma were introduced. Plasma is often referred to be the fourth state of matter, which is obtained by increasing the energy level from a solid state through the liquid and gaseous state of matter, ending in an ionized state of the gas. According to the electron temperature and ion temperature, plasma can be distinguished into thermal plasma and non-thermal plasma. Non-thermal plasma, also known as cold plasma, is a novel technology and applied to various applications. For a gas/liquid environment, plasma is generated in the gas phase, and the major reaction proceeds in the liquid phase. It is usually easier to generate plasma in a gas medium than in a liquid medium. Hence, lower energy and operating cost are required in a gas/liquid environment than as a direct discharge in a liquid. We developed a slug flow system that provides a very uniform plasma reaction field as the bubbles move regularly. Gas and liquid are introduced into a capillary glass tube by a gas valve and a solution pump, generating the bubbles and continuous gas-liquid interfaces. Copper sheets are placed outside the capillary glass tube, connecting to an alternating current (AC) pulse power supply and ground as high-voltage electrode and ground electrode, respectively. The system is powered by a high voltage of 10.0 kV (peak-to-peak). And this system has been successfully applied to the dye decomposition and synthesis of silver nanoparticles under atmospheric-pressure conditions.

In Chapter 2, cerium nitrate, magnesium chloride, and zinc chloride aqueous solutions of 1 mmol/L were used as feed solutions to synthesize corresponding metal oxide nanoparticles in the system under atmospheric conditions, respectively. Compared with traditional methods, the slug flow system provided a uniform and continuous reaction field, beneficial for nanoparticle synthesis. It also had an easy implementation and short residence time of approximately 3 s. The products were characterized by several analysis methods, including transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDS), high-resolution transmission electron microscopy (HRTEM), and Ultraviolet-visible absorption spectroscopy (UV-vis). Results showed that cerium dioxide (CeO_2), magnesium oxide (MgO), and zinc oxide (ZnO) nanoparticles were successfully synthesized by the slug flow system using atmospheric pulsed discharge plasma.

In Chapter 3, due to the ability to switch between Ce^{4+}/Ce^{3+} redox cycles, CeO_2 nanoparticles were selected as the target product to investigate the synthesis mechanism and effect of experimental factors. When pulsed discharge plasma was introduced in a gas/liquid environment, high-energy electrons accelerated in a high local electric field and ionized argon into an excited argon state, generating initial radicals. The generated radicals then contacted the water interface in the slug flow system and reacted with water molecules. Hydroxyl radicals ($OH^{\cdot}$) were generated and combined to generate more powerful oxidants, including oxygen, hydrogen peroxide, and ozone. Due to the generation of oxidizing radicals and molecules in the system, Ce^{3+} ions in the feed solution tended to be converted into Ce^{4+} ions. The Ce^{4+} ions were combined with H_2O molecules and OH^- ions to form hydroxide complexes and served as the precursors for CeO_2. The dehydration reaction tended to occur at a high local plasma temperature, triggering the crystallization of CeO_2. Instantaneous and homogeneous nucleation occurred in the slug flow system by pulsed discharge plasma. The CeO_2 nanoparticles were generated after a rapid growth process. Then the effect of different experimental factors was investigated. Besides the straight capillary glass tube, a circular capillary glass tube coil was also used as the slug flow reactor. Results showed that when using a circular capillary glass tube coil as the reactor, residence time was prolonged by approximately 3 minutes and electrodes number was increased from 2 to 15, leading to an increase in the number of produced CeO_2 nanoparticles. Due to the increasing nuclei number and time for nuclei growth, the mean size of CeO_2 nanoparticles also increased from 3.4 to 6.3 nm. Starch was added into the feed solution as a stabilizer to cap cerium ions to separate adequately the nucleation and growth process, preventing nanoparticle aggregation. With an increase in the starch concentration from 0.1 to 0.4 wt%, the amount of CeO_2 nanoparticles increased and their size distribution did not change significantly. When tetravalent cerium ions were used as the feed solution, cerium trioxide nanoparticles were also generated, which might be because a part of tetravalent cerium ions was reduced by the hydrogen ($H^\cdot$) radicals generated in the gas/liquid plasma system.

In Chapter 4, the slug flow system using gas/liquid discharge plasma was first utilized under pressurized conditions, providing a novel reaction field. The thermal temperature of the reactor under pressurized argon was measured using a compact thermal imaging camera as a maximum of approximately 40° C, a little higher than room temperature, being acceptably cold. Further insight into the chemical reactivity of the system under pressurized conditions was studied. Reactive species generated in the gas/liquid discharge plasma system were qualitatively and quantitatively analyzed. Optical emission spectra (OES) showed that the peaks of atomic argon, $H^\cdot$ radicals, and $OH^\cdot$ radicals could be observed under atmospheric and pressurized conditions. It indicated that the types of reactive species have no significant change under pressurized argon. The concentration of total oxidation species was determined by iodimetry, showing an increase with system pressure. As system pressure and density of introduced argon gas increased, collision probability between high-energy electrons and argon atoms increased, generating more initial radicals. At the same time, the number of water molecules increased with the increasing density of the feed solution, improving the contacts and reactions between initial radicals and water molecules. Hence the concentration of $OH^\cdot$ and $H^\cdot$ radicals increased, leading to an increasing concentration of further generation oxidants. Input discharge power was calculated based on the voltage and current waveforms of the system, observed by an oscilloscope. Calculated results showed that it was maintained at a steady-state under different system pressure.

In Chapter 5, the system was applied to the dye decomposition of methylene blue under pressurized argon. Methylene blue is degraded mainly by oxidation reactions to break the rings into small molecular compounds. Based on the results that the concentration of total oxidation species increased with system pressure, the ability of the system on dye decomposition was expected to be improved under pressurized conditions. The dye decomposition rates were calculated according to the result of UV-vis spectra, and the effect of experimental factors was studied. Results showed that dye decomposition rates increased greatly with the number of electrodes. The number of plasma production sites increased with the number of electrodes, leading to an increase in the number of high-energy electrons. More electrons impacted the gas atoms, resulting in the generation of more reactive species. Hence, decomposition rates increased with the number of electrodes. Then the effect of system pressure was investigated. Results showed that as system pressure increased, dye decomposition rates and energy efficiency decreased. As collision between electrons and argon gas increased under pressurized conditions, collisional energy loss increased. And improved physical effects might also increase energy loss. On basis of the similar input energy and increasing energy loss under pressurized conditions, the energy available for decomposition of methylene blue decreased, resulting in a decrease in the decomposition rates.

In Chapter 6, a conclusion of this work was made. The slug flow system using gas/liquid pulsed discharge plasma was applied successfully on the synthesis of three metal oxide nanoparticles and the decomposition of organic dyes. The developed system would be applied to other various chemical processes.